permanent dipoles at the nanometric scale. Such behaviour is not limited to octahedral clusters, as illustrated by the recently obtained $Nb_3O_2Cl_5$ built from triangular Nb_3 clusters acentrically surrounded by chlorine and oxygen ligands [14]. Unusual dielectric behaviours have been early detected in some of these original materials and a more systematic study should be essential to a better understanding of their properties.

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$(Ba,Y)(Ti,Zr,Sn)O_3$-Based PTCR Materials

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PTCR materials based on the systems $(Ba,Y)(Ti_{1-y}Zr_y)O_3$ and $(Ba,Y)(Ti_{1-y}Sn_y)O_3$ were investigated. It has been found that in the case of partial isovalent substitution of titanium ions by zirconium or tin ions, the grain size passes through a maximum at a concentration of 15 and 5 mol.% respectively. This may be attributed to the different grain growth mechanisms in the presence of a small and large amount of liquid phase. It has been shown that increasing the amount of isovalent substitution narrows the donor dopant concentration range, within which PTCR effect occurs. These results agree with the thermodynamic calculation of the range of existence of solid solutions $(Ba,Y)(Ti_{1-y}M_y)O_3$, which were regarded as a result of interaction between three phases with perovskite structure: $BaTiO_3$, $YTiO_3$ and $BaMO_3$, where M = Zr, Sn, and of the presence of complex centers Y^{3+}-Ti^{3+}, as indicated by ESR data.

Keywords: PTCR ceramic; isovalent substitution; grain size; solid solution; thermodynamic

INTRODUCTION

A characteristic feature of $(BaLn)TiO_3$-based materials with positive temperature coefficient of resistivity (PTCR) is a significant increase in resistivity over a narrow temperature range [1]. It is known that partial isovalent substitution affects the temperature range in which PTCR effect arises [2-5]. For instance, partial substitution of zirconium or tin for titanium shifts this range towards lower temperatures [4,5]. This is of a great scientific and practical interest in the development of temperature regulators with relatively low operating temperature (30-80°C). At the same time, there are no data in literature on the effect of isovalent substitutions in the titanium site of PTCR materials based on the systems $(Ba_{1-x}Y_x)(Ti_{1-y}Zr_y)O_3$ and $(Ba_{1-x}Y_x)(Ti_{1-y}Sn_y)O_3$ on the ceramic grain size and the donor dopant (yttrium) concentration range within which PTCR properties arise.

Therefore, the aim of this study was to synthesize barium titanate-based PTCR materials with isovalent substitutions of zirconium and tin for titanium and to investigate their properties.

EXPERIMENTAL PROCEDURE

Extra-pure $BaCO_3$, Y_2O_3 and TiO_2 were used as starting reagents. Zirconium and tin oxides were prepared by the thermal decomposition of hydroxides precipitated from solutions of the crystalline hydrates $ZrOCl_2 \cdot 8H_2O$ and $SnCl_2 \cdot 2H_2O$ by a 25% solution of ammonia at pH=5 and pH=8.5 respectively. The synthesis was carried out by a solid-state reaction technique. The pellet specimens about 3 mm in thickness and 10 mm in diameter were pressed and sintered at 1320-1360°C. Thermogravimetric investigations were carried out on a Q-1000 OD-102 device. XRD analysis was carried out on a DRON-3M diffractometer (Cu *Kα* radiation). ESR spectra were recorded at 20°C on a spectrometer JES-3NS-X operating at ν=9.4 GHz. The grain sizes were measured by microanalyzer JCXA Superprobe 733 (JEOL, Japan). The ohmic contacts were fabricated by firing Al paste.

RESULTS AND DISCUSSION

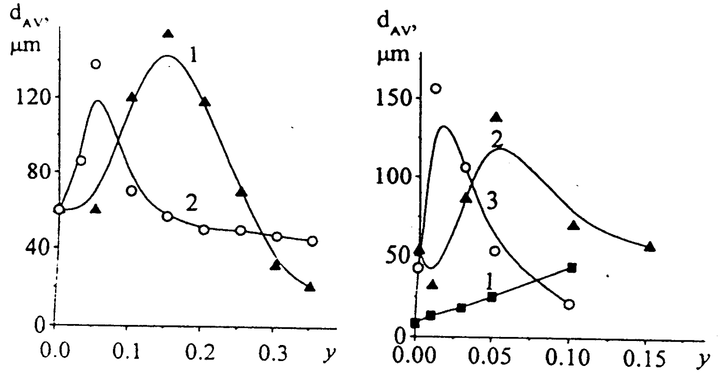
According to the results of thermal and XRD analyses, a polymorphous transformation of barium carbonate at T~820°C and its decomposition at 600-1000°C are observed in the system under investigation. At temperatures above 700°C, barium titanate ($BaTiO_3$) is formed, and at 900-1000°C the barium orthotitanate phase (Ba_2TiO_4) are formed. The presence of tin oxide or zirconium oxide during the synthesis decreases the quantity of the intermediate barium orthotitanate phase and shifts the temperature range of its existence towards lower temperatures (see table). The shift of the positions of the XRD peaks for barium titanate at 1100°C indicates the formation of corresponding solid solutions.

In the systems $(Ba_{0.996}Y_{0.004})(Ti_{1-y}Zr_y)O_3$ and $(Ba_{0.996}Y_{0.004})(Ti_{1-y}Sn_y)O_3$, the grain size passes through a maximum at $y=0.15$ ($d_{AV}=150\ \mu m$) and $y=0.05$ ($d_{AV}=130\ \mu m$) respectively (Figure 1). This character of concentration dependence may be attributed to the different grain growth mechanisms in the presence of a small (at an amount of substitution of up to 15 and 5 mol%) and large (at an amount of substitution of over to 15 and 5 mol%) quantity of liquid phase [6].

TABLE Phase composition of $BaCO_3$-Y_2O_3-TiO_2-ZrO_2 (SnO_2) mixtures after heat treatment at different temperatures

T, °C	Phase composition *		
	$0.998BaCO_3$-$0.002Y_2O_3$-TiO_2	$0.998BaCO_3$-$0.002Y_2O_3$-$0.2ZrO_2$-$0.8TiO_2$	$0.998BaCO_3$-$0.002Y_2O_3$-$0.2SnO_2$-$0.8TiO_2$
20-600	γ-$BaCO_3$, TiO_2	γ-$BaCO_3$, ZrO_2 (tetr.), TiO_2	γ-$BaCO_3$, SnO_2, TiO_2
700	γ-$BaCO_3$, TiO_2	γ-$BaCO_3$, ZrO_2 (tetr.), TiO_2	γ-$BaCO_3$, SnO_2, TiO_2
800	γ-$BaCO_3$, TiO_2, $BaTiO_3$	γ-$BaCO_3$, ZrO_2 (tetr.), $BaTiO_3$, TiO_2	γ-$BaCO_3$, SnO_2, TiO_2, $BaTiO_3$
900	γ-$BaCO_3$ (traces), β-$BaCO_3$, TiO_2, $BaTiO_3$, $BaTi_3O_7$	β-$BaCO_3$, ZrO_2 (monocl.), $BaTiO_3$, Ba_2TiO_4, TiO_2, $BaTi_4O_9$	β-$BaCO_3$, SnO_2, Ba_2TiO_4, TiO_2, $BaTi_4O_9$ $BaTiO_3$
1000	TiO_2, $BaTiO_3$, Ba_2TiO_4, $BaTi_4O_9$	$BaTiO_3$, Ba_2TiO_4, TiO_2, $BaTi_4O_9$	$BaTiO_3$, Ba_2TiO_4, TiO_2, $BaTi_4O_9$
1100	TiO_2 (traces), $BaTi_4O_9$ (traces), Ba_2TiO_4 (traces), $BaTiO_3$	TiO_2 (traces), $BaTiO_3$, $BaZrO_3$, $Ba(Ti_{1-y}Zr_y)O_3$,	$BaTiO_3$, $BaZrO_3$, $Ba(Ti_{1-y}Sn_y)O_3$,
1300	$BaTiO_3$	$Ba(Ti_{1-y}Zr_y)O_3$	$Ba(Ti_{1-y}Sn_y)O_3$

* According to the XRD results no yttrium compounds were detected



a b

FIGURE 1 Average grain size as a function of dopant content (y) of the systems:
a) $(Ba_{0.996}Y_{0.004})(Ti_{1-y}Zr_y)O_3$(1) and $(Ba_{0.996}Y_{0.004})(Ti_{1-y}Sn_y)O_3$ (2);
b) $(Ba_{1-x}Y_x)(Ti_{1-y}Sn_y)O_3$: x=0.002 (1); 0.004 (2); 0.006 (3);
T_{sint} = 1360°C.

Liquid phase is formed on isovalent substitution of zirconium or tin for titanium because of the presence of an eutectic in the systems $BaTiO_3$ and $BaZrO_3$ ($BaSnO_3$) [7,8]. When the yttrium content in PTCR solid solutions $(Ba_{0.996}Y_{0.004})(Ti_{1-y}Sn_y)O_3$ is increased, the trend of the plot of average grain size (d_{AV}) versus the amount of isovalent substitution (y) persists qualitatively, but the d_{AV} maximum shifts towards higher y value (Figure 1b).

An examination of ESR spectra of the ceramics $(Ba_{0.996}Y_{0.004})(Ti_{1-y}Zr_y)O_3$ and $(Ba_{0.996}Y_{0.004})(Ti_{1-y}Sn_y)O_3$ showed the presence of paramagnetic centers Ti^{3+}-Y^{3+} with $g \approx 1.963$ (Figure 2). These centers were first detected in the PTCR ceramics $(Ba_{1-x}Ln_x)TiO_3$ (Ln = rare-earth element), and their presence was attributed to the participation of the perovskite phase $LnTi^{3+}O_3$ in the formation of PTCR materials $(Ba_{1-x}Ln_x)(Ti^{4+}_{1-x}Ti^{3+}_x)O_3$ [9].

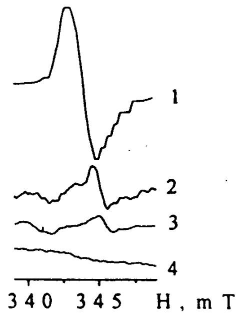


FIGURE 2 ESR spectra of the ceramics $(Ba_{0.996}Y_{0.004})TiO_3$ (1), $(Ba_{0.996}Y_{0.004})(Ti_{0.95}Zr_{0.05})O_3$ (2) $(Ba_{0.996}Y_{0.004})(Ti_{0.8}Zr_{0.2})O_3$ (3), $(Ba_{0.996}Y_{0.004})(Ti_{0.65}Zr_{0.35})O_3$ (4) at 20°C. T_{sint}=1360°C.

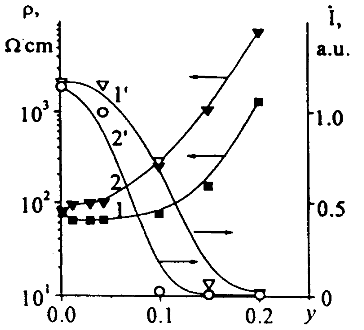


FIGURE 3 Resistivity ρ (1,2) and integrated ESR signal intensity (I) of Ti^{3+} Y^{3+} centers (1',2') *vs.* the dopant content y of the ceramics $(Ba_{0.996}Y_{0.004})(Ti_{1-y}Zr_y)O_3$ (1,1') and $(Ba_{0.996}Y_{0.004})(Ti_{1-y}Sn_y)O_3$ (2,2') at 20°C. $T_{sint.}$=1360°C.

Increasing the isovalent substitution in the systems under investigation decreases the intensity of ESR signal from impurity centers Ti^{3+}-Y^{3+} (Figure 3) and narrows the yttrium concentration range within which PTCR properties arise (Figure 4). The concentration of isovalent dopant (Zr or Sn) at which the ESR signal from Ti^{3+}-Y^{3+} centers disappears corresponds to the concentration at which rapid resistivity increase begins (See Figure 3).

To explain the observed relations, we carried out a thermodynamic calculation of the concentration range of existence of PTCR solid solutions at different sintering temperatures. PTCR solid solutions $(Ba^{2+}_{1-x}Y^{3+}_x)[(Ti^{4+}_{1-y}M^{4+}_y)_{1-x}Ti^{3+}_x]O_3$ (where M = Zr, Sn) were regarded in the calculation as resulting from the interaction of three phases with perovskite structure:

$$(1-x)(1-y)BaTi^{4+}O_3 + y(1-x)BaM^{4+}O_3 + xY^{3+}Ti^{3+}O_3 \rightarrow$$
$$\rightarrow (Ba^{2+}_{1-x}Y^{3+}_x)[(Ti^{4+}_{1-y}M^{4+}_y)_{1-x}Ti^{3+}_x]O_3$$

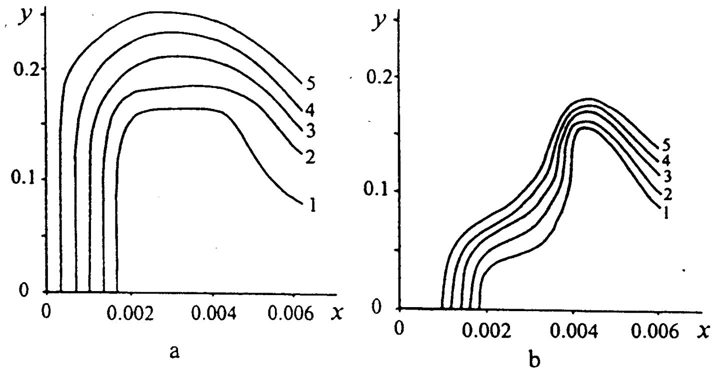


FIGURE 4 a) Resistivity isolines of the ceramic $(Ba_{1-x}Y_x)(Ti_{1-y}Zr_y)O_3$ at 500 Ω·cm (1); 1 000 Ω·cm (2); 1 500 Ω·cm (3); 2 000 Ω·cm (4); 2 500 Ω·cm (5);
b) Resistivity isolines of the ceramic $(Ba_{1-x}Y_x)(Ti_{1-y}Sn_y)O_3$ at 1 000 Ω·cm (1); 2 000 Ω·cm (2); 3 000 Ω·cm (3); 4 000 Ω·cm (4); 5 000 Ω·cm (5).

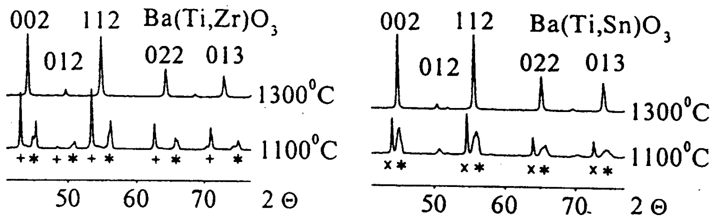


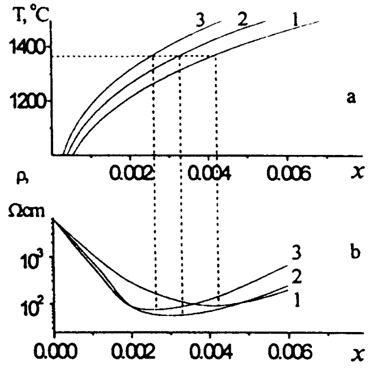
FIGURE 5 XRD of $BaCO_3$-Y_2O_3-TiO_2-MO_2 systems after heat treatment at different temperatures; $BaTiO_3$ (*); $BaZrO_3$ (+); $BaSnO_3$ (x). No yttrium compounds were detected.

The presence of the intermediate phases $BaTi^{4+}O_3$ and $BaM^{4+}O_3$ (where M = Zr, Sn) at 1100°C is indicated by the results of XRD investigation of the phase changes that take place during the synthesis of PTCR materials (Figure 5). The possible participation of the $Y^{3+}Ti^{3+}O_3$ phase in the formation of PTCR materials was inferred from the presence of signals from centers Ti^{3+}-Y^{3+} in ESR spectra.

The methodology proposes in refs [10,11] was employed in the thermodynamic calculation. The concentration range (x) of isomorphic miscibility is related to synthesis temperature (T) by the Becker equation [10]:

$$T = -\frac{1-2\cdot x}{\ln\cdot[x/(1-x)]}\cdot\frac{Q}{R} \qquad (1)$$

where Q is the energy of phase mixing and R the universal gas constant.



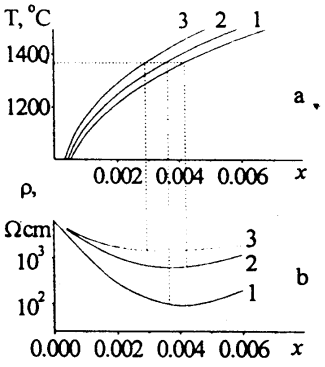


FIGURE 6 Calculated ranges of existence of substitutional solid solutions (a) and experimental plots of the resistivity (b) of PTCR ceramics $(Ba_{1-x}Y_x)(Ti_{1-y}Zr_y)O_3$ vs. x. y=0 (1); 0.05 (2); 0.1 (3). T_{sint}=1360°C.

FIGURE 7 Calculated ranges of existence of substitutional solid solutions (a) and experimental plots of the resistivity (b) of PTCR ceramics $(Ba_{1-x}Y_x)(Ti_{1-y}Sn_y)O_3$ vs. x. y=0 (1); 0.05 (2); 0.1 (3). T_{sint}=1360°C.

When associates, e.g. Y^{3+}-Ti^{3+}, arise in solid solution, the energy of mixing is calculated from the equation [11]:

$$Q = (k \cdot c) \cdot m \cdot n \cdot Z_1 \cdot Z_2 \left(\frac{(r_1 + r_2) - (r_3 + r_4)}{x_1 \cdot (r_1 + r_2) + x_2 \cdot (r_3 + r_4) + 2r_0} \right)^2 \quad (2)$$

where k is the number of elementary substitutions in one act of solid solution formation, c is empirical parameter, which dependent on crystal structure of solid solution end members (for perovskites 27 [11]), m the number of ions in the formula unit ABO_3, n the coordination number at substituional site, Z_1 and Z_2 are the formal ionic charges of the substituent and substituted cations respectively, x_1 and x_2 the contents of the substituent and substituted cations respectively ($x_1 + x_2 = 1$), r_i the ionic radii of cations in perovskite phases of the types $A^{(1)}B^{(2)}O_3$ and $A^{(3)}B^{(4)}O_3$, which form the solid solution $(A^{(1)}A^{(3)})(B^{(2)}B^{(4)})O_3$, and r_0 the ionic radius of oxygen.

The results of calculations obtained according to equations (1) and (2) showed that increasing the zirconium and tin content decreases the yttrium concentration range in which PTCR solid solutions $(Ba_{1-x}Y_x)(Ti_{1-y}M_y)O_3$ (where M = Zr, Sn) are formed, which is in good agreement with experimental data (Figure 6,7).

CONCLUSION

Thus, the investigations carried out by us showed that increasing the degree of isovalent substitution for titanium in $(Ba^{2+}_{1-x}Y^{3+}_{x})[(Ti^{4+}_{1-y}M^{4+}_{y})_{1-x}Ti^{3+}_{x}]O_3$ system (M = Zr, Sn) leads to a narrowing of the concentration range of yttrium as donor dopant, within which PTCR properties arise. These results are in good agreement with thermodynamic calculations if solid solutions are regarded as resulting from the interaction of three phases with perovskite structure: $Ba^{2+}Ti^{4+}O_3$, $Y^{3+}Ti^{3+}O_3$, $BaM^{4+}O_3$. A change in ceramic grain size in the case of partial isovalent substitution in titanium site may be due to different grain growth mechanisms in the presence of a small and large quantity of liquid phase.

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